Metal Sensitizer in Chemically Amplified EUV Resist: a Study of Sensitivity Enhancement and Dissolution

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Metal containing non-chemically amplified EUV resists have gained growing attention in recent years due to superior line space patterning performance, high etch resistance and ultrahigh sensitivity. Their favorable performance and sensitivity are believed to correlate with metals-light interactions. However, there is very few report of metal containing resists on EUV contact holes patterning. In this work, we study an alternative type metal containing resist, which utilizes conventional CAR with metal salts as sensitizer. CAR with metal sensitizer has shown enhanced sensitivity and slightly increase LCDU, yet reduced LWR is also observed in some cases. Therefore, this work is dedicated to studying the influences of metal sensitizer on resist physical properties and the underlying sensitivity enhancement mechanism.

Keywords: EUV, Metal sensitizer, LCDU, Sensitivity, Dissolution

1. Introduction

Extreme ultraviolet lithography at the wavelength of 13.5 nm is one of the most promising candidate to continue “Moore’s law” of shrinking in critical dimension. However, the well known tradeoff of sensitivity, roughness and resolution (RLS) continues to be a huge challenge for EUV lithography. Conventional chemically amplified resists (CAR) have advantages of mature manufacturing compatibility, however higher dose is often needed to reduce photon shot noise effects and to improve LWR or LCDU [1–3]. LWR and LCDU of state-of-art EUV resists are still far from manufacturing requirements. On the other hand, metal containing resists have attracted a lot of attention in recent years due to superior line space patterning performance [4], high etch resistance [5] and ultrahigh sensitivity[6–8]. Metal oxide resists utilize a sol-gel mechanism to form condensed metal oxide network [9], while nanoparticle resists first studied by Cornell Ober group utilize ligand removal or exchange to achieve solubility switch [10]. The drawback of metal oxide resist is relatively low sensitivity, while nanoparticle resists lack enough resolution. Although these metal containing resist utilize novel patterning mechanism and smaller building blocks, RLS tradeoff is still observed [11]. In addition, due to relative short history of the metal resist, integration of these novel metal resists into high volume manufacturing requires tedious efforts in resist optimization and risk management.

Metal sensitizer in chemically amplified resist offers a compromise solution between CAR and pure metal oxide resists [12]. Due to very small percentages of metal additives, the process of metal sensitizer resist is the same as the process of CAR. Yet, such small portion of metal salts improves sensitivity by 10%-30%. With low metal sensitizer loading, a 18% sensitivity improvement was observed with only 2% of LCDU increase [12]. Furthermore, LWR reduction was observed in one medium metal sensitizer loading with almost 30% reduction. Therefore, studying the sensitivity enhancement mechanism and metal additive’s influence on physical behavior such as dissolution will help us to gain understanding to design more efficient resists and potentially explore a way to reduce LWR and LCDU while maintaining high sensitivity.

2. Experimental

EUV exposures were performed in Imec and Veldhoven using ASML NXE:3300B and annular
illumination condition. TEL CLEAN TRACKTMT LITHIUS ProTM Z-EUV tool was used. 35 nm resist film were freshly coated on AL412 20 nm underlayer on Si and soft baked at 105 °C for 60 s. OPD262 static 30s development and SPC683 rinse were applied after PEB. The target feature for this study is 26 nm orthogonal CH at 52 nm pitch with 0% reticle bias. LCDU is the averaged 3 sigma variation of 81 contacts holes of 9 exposed fields. SEM were performed on the HITACHI CG-5000 at 500 V an 8 pA.

Static contact angle was measured using dataphysics OCA 230L. TOF-SIMS spectra was measured using TOFSIMS IV from ION-TOF GmbH dual beam configuration. Cross-section scanning electron inspections (X-SEM) were performed using a Hitachi SU-8000 system, after Pt sputter-coating for contract enhancement. Absorption at EUV wavelength and total electron yield (-30 V) bias are measured in Elettra synchrotron (Trieste, Italy) and the detail can be found in reference [13,14]. Resist film (approximately 30 nm) for light-matter interaction measurements are coated on SiN and etched back.

3. Results and discussion

3.1. Contact angle

![Fig. 1. Static water contact angle of organic underlayer (AL412) and resists without (A-1) and with metal loading (M-1, M-2, M-3).](image1)

Static water contact angle of organic underlayer (AL412), reference resists without metal (A-1), metal sensitizer resist with 1-times, 2-times and 3-times metal loading (M-1, M-2, M-3) are shown in Fig. 1. Contact angle of AL412 and reference resist A-1 are 66° and 69° respectively. While the contact angles of metal sensitizer resists increase to 75°, regardless of metal loading. Such increase might be due to the nonpolar anion group of the metal sensitizer molecule. Increase in water angle leads to slight reduced work of adhesion [15], which might play a role in the patterning failing during TMAH development. It is also noticed that the standard variation of water contact angle decreases with metal loading, which might be due to the nonuniform distribution of metal sensitizer.

3.2. Chemical uniformity

![Fig. 2. ToF-SIMS analysis of metal distribution in depth profile.](image2)

To study the distribution of metal sensitizer in the resist, dual beam time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements were performed. Intensity of secondary ions are plotted against the sputtering time. The position at 25 s sputtering time is denoted as the air-resist interface due to a short stabilization period and the position at 175 s is denoted as Si-resist interface due to the sudden increase in the Si concentration. As shown in Fig. 2,
concentration of metal progressively increases from top to bottom, which might due to the higher density of metal salts. The intensity of metal at different depth is proportional to total metal loading. Therefore, the higher metal loading, the less chemical noise is.

Sulfur and fluorine distribution depth profile are obtained as well (Fig. 3). As sulfur only exists in PAG molecule in A-1, the distribution of sulfur reflects the distribution of PAG molecules in A-1. A slight increase in sulfur content is observed in A-1 from 25 s to 100 s sputter time. Although PAG is bounded to polymer back bond in this study, such trend suggests that PAG concentration near the surface is lower than the bottom.

On the other hand, the distribution of fluorine shows a significant increases between 160s and 180s sputter time. As fluorine atoms also only exists in PAG molecules in A-1, the distribution of fluorine confirms non-uniform distribution of PAG. In Section 3.3, we examined the impacts of PAG and sensitizer distribution on resist profile by cross-section SEM.

3.3. X-SEM

Cross-section images of metal sensitizer resists contact hole patterning are shown in Fig. 4. All the contact holes are thoroughly open from to bottom. Therefore, the metal distribution depth profile does not impact the resist profile. However, significant top loss is observed at the surface of resist with increasing metal loading, especially for M-2 and M-3, which might be related to resists dissolution behavior.

3.4. Dissolution behavior

Resists were coated on a HDMS primed Si wafer without any underlayer and then were flood exposed to EUV radiation by NXE3300B scanner. Subsequently, dissolution rates of resists are monitored by dissolution rate monitor (DRM) (Fig. 5).

All resists were readily dissolved within one second at the maximum exposure dose (dose to size for P44 line space pattern), which is fast enough for a 30s-development process. The maximum dissolution rate ($R_{max}$) is summarized in Fig. 6A. $R_{max}$ surprisingly jumps from 37 nm/s to over 200 nm/s with metal sensitizer considering the same polymer used and $R_{max}$ increases progressively with metal loading.

With medium exposure doses, resist dissolved within 2 s-40 s. Unlike most of CARs, which dissolve fast in the beginning and slow near the bottom, the resists in this work showed reversed behavior. They dissolve slow in the beginning and
fast near the bottom, as seen from A-1 exposed at 5 mJ/cm², M-2 exposed at 3.5 mJ/cm² and 2.5 mJ/cm² and M-3 exposed at 2.5 mJ/cm². Such behavior might be important to maintain a thoroughly open contact hole profile. The faster dissolution rate at the bottom of resist film might be due to the faster deprotection at the bottom given high PAG concentration, however, the underlying reason is unknown.

With metal loading $R_{\text{min}}$ increase from 0.025 nm/s (A-1) to 0.048 nm/s (M-1) to 0.1 (M-2 and M-3) (Fig. 6B). Simultaneous increase in both $R_{\text{min}}$ and $R_{\text{max}}$ is likely due to high solubility of metal sensitizer in TMAH. Metal sensitizer first dissolves in TMAH solution, consequently resists disintegrate, thus increasing dissolution rate. The increase in $R_{\text{min}}$ with metal loading should be blamed for the top loss of the resist pattern observed in Fig.3. Nonetheless, M-1 benefits from the more significant increase in $R_{\text{max}}$, therefore dissolution contrast of M-1 is above 4000, higher than A-1 (~1100), M-2 (2400) and M-3 (2000). Higher dissolution contrast is beneficial for the dense line patterns [16] and slightly increase $R_{\text{min}}$ might slight help reducing LWR [17]. Moreover, we have observed that the exposed M-1 at medium dose are completely dissolved at 30 second development, which is favorable for reducing scuming or nano-bridging formation.

3.5. EUV light matter interactions

Extinction coefficient ($k$) and transmission obtained in Elettra beamline are averaged over measurements from more than 6 positions. Absorbance coefficient can be calculated from extinction coefficient using the following equation.

$$\mu(\mu m^{-1}) = 4\pi k/\lambda$$  \hspace{1cm} (1)

Theoretical absorption of metal sensitizer molecule calculated from the following equation:

$$\mu = \frac{N_A \rho \lambda}{MW} \sum x_i \sigma_{a_i}$$ \hspace{1cm} (2)

where is $\mu$ the EUV absorption coefficient of the given compound, $\rho$ is the density, MW is the molecule weight of a compound, $x_i$ is the number fraction of component i and $\sigma_{a_i}$ is the atomic photo-absorption cross section. Theoretical absorption of sensitizer molecule is 6.4 $\mu m^{-1}$. As seen in Fig. 7, the reference resist without metal sensitizer has EUV absorption at 6.34 $\mu m^{-1}$, slightly higher than previously reported EUV resists [18]. Counterintuitively, as more metal sensitizers are added to resists, absorption decreases surprisingly (Fig. 7), which suggests the real EUV absorption of metal sensitizer is lower than theoretical calculation. Absorption is not the key to determine sensitivity.
Total electron yield (TEY), namely the number of generated electron per incident photon, measures the current of electrons escapes from the surface of resist film at -30V bias. Therefore, we assumed resists are uniform throughout the film. TEY of A-1, M-1, M-2 and M-3 during 1st and 2nd are shown in Fig. 8. Unlike most of the most EUV CAR and metal containing resists, 20% decrease of TEY after 1st scan was observed for all samples, suggesting that EUV radiation changes the chemistry of electron generating materials. It is believed that EUV photons generates electrons mainly through the ionization of the polymer [19,20], yet in this case PAG is very likely to have an important contribution in electron generation.

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It is also worth noticing that although TEY increases with increasing metal loading, TEY of M-1 decreases from non-metal sensitizer containing A-1. It is certain that metal sensitizer indeed contributes to the electron generation as TEY increases with increasing metal loading. Yet, the addition of metal might change the electrical properties of resists film, therefore from A-1 to M-1, not all the electrons generated were driven out and measured by the picoamperometer.

Meanwhile, dielectric constant might decrease with metal sensitizer addition. Previous simulation study showed that a lower dielectric constant provide less electric shielded by surrounding molecules dielectric materials, thus allowing large resolution blur [21,22]. Therefore, the dielectric constant might be one of the reason for high LCDU. Yet, further experiments are needed to confirm this hypothesis.

Figure 9 shows the secondary electron yield (SEY), namely the number of generated electron per absorbed photon, which can be calculated from the following equation

\[
SEY = \frac{TEY}{(1 - \exp\left(-\frac{\pi k t_{eff}}{\lambda}\right)}
\]  

(3)

where \(t_{eff}\) is the effective electron escape length [23]. SEY suggests the electron generation efficiency from absorbed photons. Although metal sensitized resists has lower absorption, the higher TEY rendered higher SEY as a result of EUV light metal interaction and/or lower dielectric constant. The higher SEY explains the higher sensitivity of the metal sensitizer resists. Yet, potentially higher secondary electron diffusion might cause a decrease in LCDU shown in previous report. Previous studies in Imec shows that SEY of EUV CAR has SEY of 4-5 electrons per absorbed photon [14] while metal oxide resist has SEY of 2-3 electrons per absorbed photon. SEY of our resists are closer to SEY of metal containing resist.

### 3.6. EUV patterning

Table 1. List of metal sensitized resists for EUV patterning

<table>
<thead>
<tr>
<th>Resist Code</th>
<th>PAG</th>
<th>Quencher</th>
<th>ALU</th>
<th>Metal</th>
<th>Sensitivity Improve</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>x1</td>
<td>x1</td>
<td>x1</td>
<td>x0</td>
<td>0</td>
</tr>
<tr>
<td>M-1</td>
<td>x1</td>
<td>x1</td>
<td>x1</td>
<td>x1</td>
<td>28%</td>
</tr>
<tr>
<td>M-2</td>
<td>x1</td>
<td>x1</td>
<td>x1</td>
<td>x2</td>
<td>30%</td>
</tr>
<tr>
<td>M-3</td>
<td>x1</td>
<td>x1</td>
<td>x1</td>
<td>x3</td>
<td>34%</td>
</tr>
<tr>
<td>M-4</td>
<td>x1</td>
<td>PDQ3</td>
<td>x1</td>
<td>x2</td>
<td>22%</td>
</tr>
<tr>
<td>M-5</td>
<td>x1</td>
<td>PDQ4.5</td>
<td>x1</td>
<td>x1</td>
<td>10%</td>
</tr>
<tr>
<td>M-6</td>
<td>x1</td>
<td>x2</td>
<td>x1</td>
<td>x2</td>
<td>20%</td>
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<tr>
<td>M-7</td>
<td>x1</td>
<td>x3</td>
<td>x1</td>
<td>x2</td>
<td>28%</td>
</tr>
<tr>
<td>M-8</td>
<td>x1</td>
<td>x1</td>
<td>x1.3</td>
<td>x2</td>
<td>23%</td>
</tr>
<tr>
<td>M-9</td>
<td>x1</td>
<td>x1</td>
<td>Hydrophobic</td>
<td>x2</td>
<td>19%</td>
</tr>
</tbody>
</table>

\(^{a}\) Results from A-1, M-1, M-2 and M-3 is reproduced from Ref [12].
In order to test the EUV patterning capability of metal sensitizer resist and understand their sensitivity and LCDU relationships, metal sensitizer was added to different resist formulations as listed in Table 1. These resist formulations include different quencher loadings, quencher types and acid labile units (ALU). Sensitivity improvement from their non-sensitizer formulations counterparts is observed for all samples. Metal sensitizer in photo-decomposable quencher (PDQ) samples showed less sensitivity improvements, which might due to high quencher loading.

SEM images of pitch 52 nm contact holes for M-1, M-2 and M-3 is reported in Ref 12. SEM images of EUV patterning results of M-4 to M-9 are shown in Fig. 10. M-4 to M-7 are high quencher loading samples, therefore as seen in Fig. 10, contact holes are relative uniform. However, M-8 and M-9 for different ALU are low dose samples, hence contact holes are much less uniform and even missing contact holes can be seen in M-9.

LCDU and sensitivity relationship are summarized in Fig. 11. All the samples appear to follow the LCDU-sensitivity tradeoff. The weaker LCDU performance at low dose should be at least partially blamed to the increased photon shot noise. Yet M-1 and M-2 demonstrated that with low quencher loading, LCDU can be maintained with reducing doses by adding small percentage of metal sensitizer. M-4 demonstrated that with higher quencher loading, better LCDU comparison to reference can be obtained at the same dose.

4. Conclusion

Metal sensitzers were shown to effectively improve sensitivity of chemically amplified resist while maintaining LCDU and LWR [12]. In this work, we further studied the physical properties and light matter interaction of metal sensitizer resists. We found metal sensitizer makes surface of resist film more hydrophobic and dissolution rate of exposed and unexposed resist much faster. Yet, the increase in $R_{\text{min}}$ resulted in top loss. We also found that metal concentration increases from top to bottom, but such distribution does not affects the resist cross-section profile.

In order to understand the mechanism of sensitivity enhancement, absorption coefficient, total electron yield of metal sensitizer resist are measured and secondary electron yield are calculated. We found the absorption of metal sensitizer is lower than the theoretical calculation and even lower than the reference resists itself. Yet, metal sensitizer helps generating more electrons. With low absorption and high electron yield, SEY, namely the electron generation efficiency, increases with metal loading, thus leads to sensitivity improvement. Absorption is not the key to sensitivity but the electron generation efficiency has positive relationship to sensitivity improvement.

Meanwhile a 20% reduction of TEF was observed from A-1 to M-1 which might due to the changes in resist electric properties. Yet, this needs to be confirmed with further experiments.

Lastly, EUV patterning of metal sensitizer in different resist formulations at pitch 52 nm contact hole were obtained. Although sensitivity improvement still trades off with LCDU, metal sensitizer provide an extra knob to improve RLS.

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References